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Review on the development of natural dye photosensitizer for dye-sensitized solar cells

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ABSTRACT

Dye-sensitized solar cell (DSSC) provides credible alternative concept for inorganic solid-state photovoltaic devices. The conversion efficiency of DSSC is mainly based on the dye coated on the porous semiconductor TiO_2 film. The use of natural dyes in solar cells is a promising development to this technology because it cuts down the high cost of noble metals and chemical synthesis. Therefore, this type of solar cell has attracted considerable attention from the academic and industrial communities. Numerous kinds of pigments, such as anthocyanin, carotenoid, chlorophyll, and flavonoid, extracted from various plant components, such as leaves, fruits, and flowers, have been tested as sensitizers. The photostability of the DSSC sensitizer material must be capable of undergoing many redox cycles without decomposition, and must also have the ability to carry attachment groups, such as phosphonate or carboxylate, to promptly graft it to the TiO_2 oxide. This paper highlights and discusses the development of natural dye photosensitizers and the mechanisms affecting the dye stability.

Contents

1. Background and development of dye-sensitized solar cells

Solar energy is the source of nearly all energy on earth. Among all the renewable power sources, solar energy is the most easily exploitable, inexhaustible, quiet, and adjustable to enormous applications [1,2].

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Photovoltaic (PV) is a device that directly converts sunlight into electricity without pollution, sound, or moving parts, thereby making it long lasting and dependable. PV is an elegant method that takes advantage of the sunlight [3,4]. The basis on the mechanism of PV devices depends on the charge concept that separates at an interface of two materials with different conduction mechanisms [5]. The history of PV surfaced in the 19th century when Charles Fritts fabricated the primitive photovoltaic cell composed of selenium and a thin layer of gold [6,7]. After 1873, the first panchromatic film, rendering realistic images into black and white, followed the great work of Hermann Wilhelm Vogel, in which he discovered a method for increasing the photographic emulsion sensitivity and associated silver halide emulsions with dyes to produce black and white photographic films. Silver halides are insensitive to much of the visible light because they have band gaps at 2.7–3.2 eV. This achievement can be considered the first significant study on the dye sensitization of semiconductors [8,9].

In 1905, Albert Einstein described how photon absorption causes photoelectric effect, and was awarded the Nobel Prize in 1921 [5]. Russel Ohl fabricated silicon solar cell in 1941. In 1954, Bell Lab announced the production of silicon solar cells with over 6% efficiency [10]. The schematic of the silicon cells, which are merely silicon (semiconductor) p–n junctions, is shown in Fig. 1. When n-type and p-type semiconductors are joined, a motion of electrons and holes across the junction occurs until equilibrium is reached. This phenomenon is called the equalization of the Fermi energy level in the materials. N-type semiconductors obtained through the addition of pentavalent impurity atoms (doping), such as phosphorus, arsenic, and antimony, share free electrons, thereby significantly increasing silicon conductivity. The addition of trivalent impurity atoms, such as boron, gallium, and aluminum, which has one valence electron less than the silicon atoms, creates P-type semiconductors [11,12].

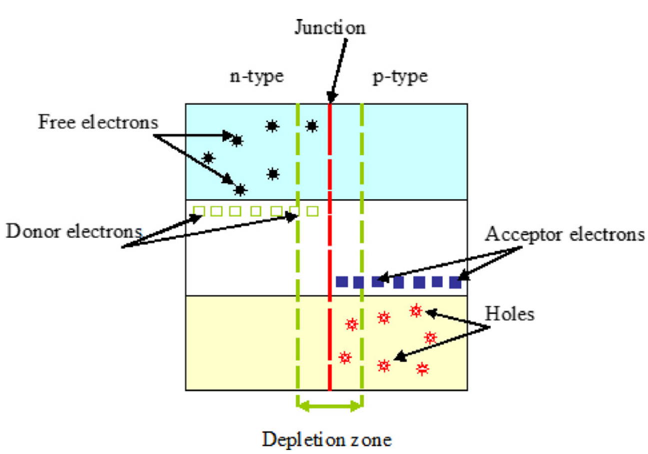


Fig. 1. Schematic diagram of a crystalline Silicon cell [19].

First generation is a term that refers to the p-n junction photovoltaic, typically made from mono- and poly-crystalline silicon doped with other elements [13,14]. Both single (mono) and multi (poly)-crystalline photovoltaic require long fabrication processes and enormous amount of silicon materials. The PV devices that have recorded the highest efficiency are the first generation cells based on mono crystalline silicon. However, these cells have high fabrication cost and composition [15]. From 1954 to 1960, Hoffman developed a method to increase the PV cell efficiency from 2% to 14% [16].

Thin film photovoltaic cells are the second generation of PV devices based on amorphous polycrystalline compound semiconductors. Historically, amorphous silicon (A-Si), cadmium telluride (CdTe), and copper indium gallium selenite (CIGS), and to date, thin-film polycrystalline silicon, have been regarded as key thin-film candidates, among which the CdTe thin film technology is the most expensive [17,18]. The three types of thin film cell structures include mono or single junction, double or twin junction, and multiple junctions. The main difference among these structures is the number of p–i–n junction layers. Depositing thin material layers with various band gaps improves cell efficiency, but increases cost due to several processes or methods involved in depositing each layer of materials during fabrication.

However, the efficiency of these cells is less than the efficiency of wafer-based silicon solar cells that currently dominate the commercial PV market [19]. Numerous scientists are working on the development of thin film devices that decrease the high cost of production and improve the efficiency of cells [20,21]. The first and second generations of PV devices are fundamentally constructed from semiconductor materials [22,23].

The development of low-cost PV cells has been the topic of intensive research over the last three decades. The third generation PV cell technologies differ from first and second generation technologies by looking forward to optimize the efficiency and notably decrease costs [24–26]. Most of the third generation solar

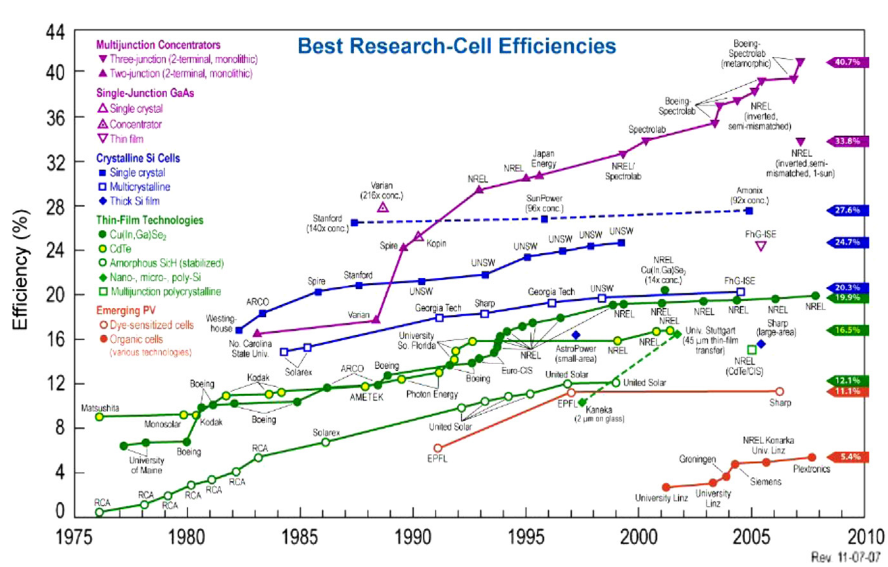


Fig. 2. Chart of photovoltaic cell developments from 1975 to 2010 [5].

cells are still in the research process, and tend to contain dye-sensitized solar cell (DSSC), heterojunction cells, quantum dot cells, polymer solar cells, and hot carrier cells [27–29].

DSSC is a unique device for the conversion of visible light into electricity based on wide band gap semiconductor sensitization, and belongs to a group of thin film cells [30–33]. The history of dye-sensitized solar cell started in 1972 when a chlorophyll-sensitized zinc oxide (ZnO) electrode was developed [34]. Carlson and Pankove reported the first amorphous silicon solar cell in 1976 with an efficiency of 2.4%, which was later increased to 4% [35]. In the following years, DSSC has become an attractive subject in solar energy cell research from both applied and fundamental points of view. The main dilemma was that a single layer of dye molecules on a surface enabled 1% incident sunlight absorption [36]. In 1990, at the Ecole Polytechnique Federale de Lausanna (EPFL), Grätzel and his co-workers succeeded in developing a new type of solar cell, known as DSSC or Grätzel cell [37–39], which mimics the photosynthesis in plants by sensitizing nano-particulate titanium dioxide (TiO_2) films with novel ruthenium (Ru) bipyridyl complex.

In DSSCs, charge separation by kinetic competition is similar to natural photosynthesis, whereas solar cell charge separation takes place by the movement of charge carriers or drift current in the p–n junction [15]. In addition, the dye in DSSC or photoelectrochemical particle substitutes the chlorophylls; the nano-structured semiconductor layer substitutes the nicotinamide adenine dinucleotide phosphate; and carbon dioxide acts as the electron acceptor. Furthermore, the electrolyte substitutes the water, whereas oxygen acts as the electron donor and oxidation product [40–42].

The performance of DSSC mainly relies on the dye sensitizer. The dye absorption spectrum and the anchorage to the surface of the semiconductor TiO_2 are important parameters for determining DSSC efficiency [43]. Currently, inorganic solid-state junction devices that are usually made of silicon are dominating the photovoltaic field and industry because of their cell efficiency, as shown in Fig. 2. However, the dominance of solid-state junction devices is now being challenged by the emergence of DSSCs. These nanocrystalline material-based devices and conducting thin films can potentially replace the conventional solid-state devices [3,44,45]. By far, the efficiency of DSSCs sensitized by Ru compound adsorbed on the semiconductor nanocrystalline TiO_2 has reached 11–12% [46,47].

2. Structure of DSSCs

A schematic of the structure of DSSCs is shown in Fig. 3. DSSC differs from other solar cell devices both by its basic construction and the physical processes behind its operation. In contrast to the first and second generation PV devices based on solid-state semiconductor materials, the typical DSSC arrangement combines liquid and solid phases. DSSC is composed of a transparent conducting glass electrode (anode) that allows the light to pass through the cell [48,49]. Clear glass substrates are used as electrode substrates because of their low cost, availability, and high transparency in the visible spectrum. The fluorine tin dioxide $F{:}SnO_2$ coating has a transparent conductive face. The mesh titanium nanoparticle TiO_2 acts as a dye container, and provides electron passage through the cell. The TiO_2 particles are coated with dye molecules (light sensitizer) that convert photons into excited electrons and cause current flow. The dye is surrounded by the electrolyte layer (usually iodide) that acts as a source to compensate the lost electron. The counter electrodes (cathode) on the other side of the cell are typically coated with graphite or platinum.

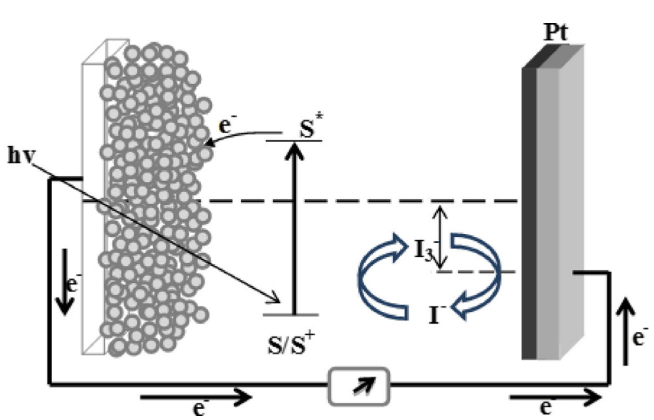


Fig. 3. Schematic structure and principle of operation of DSSC [9].

3. Operation principle of DSSCs

The absorption of light photon in DSSC occurs in the dye molecule layer [50]. Nanocrystalline TiO_2 provides the indispensable major surface area for dye molecule absorption. The dye molecules (sensitizers) collect photons and produce the excited electrons (S*) from the highest occupied molecular orbital in the ground state to the lowest unoccupied molecular orbital (LUMO) in the excited state (Fig. 3). This process is described by Eq. (1). The dye injects an excited electron into the conduction band of nanoporous TiO_2 film and ZnO or SnO_2, which are used in solar cells [51–53]. The dye molecules that lost an electron are then oxidized (Eq. 2). The injected electron travels through the nanoporous TiO_2 thin film toward the conductive electrode (anode), and is simultaneously extracted to a load where the work performed is delivered as an electrical energy (Eq. 3). The electron, finally travels back through an external load and reaches the cathode (counter electrode). The electron is transferred to the electrolyte at the cathode. The electrolytes containing I^-/I_3^- are used as brokers between the cathode (carbon plated counter electrode) and the TiO_2 photoelectrode. Thus, the oxidized dye receives electron from I^- ion redox to replace the lost electron [54–56], and the iodide molecules are then oxidized into Tri-iodide ions (I_3^-). This process is described by Eq. (4). The I_3^- ions float around until they reach the cathode to compensate its missing electron from the counter electrode. The I^- is regenerated by the reduction of I_3^- at the cathode, and the circuit is completed by the immigration of electron through the external load (Eq. 5) [5,57,58]. The electron motion in the conduction band of the wide band gap semiconductor nanoporous TiO_2 film is escorted by the charge-compensating cation diffusion in the electrolyte relative to the semiconductor surface. Therefore, the generation of electric power in DSSC does not cause permanent chemical transformation [37,59].

$$S + \text{photon} \rightarrow S^* \quad \text{Absorption} \tag{1}$$

$$S^* + TiO_2 \rightarrow e^-(TiO_2) + S^+ \quad \text{Injection process} \tag{2}$$

$$e^-(TiO_2) + C.E. \rightarrow TiO_2 + e^-_{(C.E.)} + (\text{electrical energy}) \quad \text{Energy generation} \tag{3}$$

$$S^+ + 3/2\, I^- \rightarrow S + 1/2\, I_3^- \quad \text{Regeneration of dye} \tag{4}$$

$$1/2\, I_3^- + e^-_{(C.E.)} \rightarrow 3/2\, I^- + C.E. \quad \text{Regeneration reaction} \tag{5}$$

Table 1
Photoelectrochemical parameters of commercial dyes with efficiencies over 5% based DSSC using TiO_2 semiconductors oxide.

Dye	λ_{max} (nm)	J_{sc} ($mAcm^{-2}$)	V_{oc} (V)	FF	η (%)	Reference
Polyene-diphenylaniline, D5	476	11.9	0.66	0.68	5.1	[91]
Hemicyanine, HC-1	535	13.9	0.52	0.57	5.2	[92]
Thienylflourene	538	12.47	0.65	0.65	5.23	[93]
4-*N*,*N*-diphenylamine-benzaldehyde	406	11.33	0.86	0.57	5.56	[94]
Phenothiazine, Z4	470	10.35	0.80	0.69	5.73	[95]
Indoline, Ind 1	491	17.76	0.60	0.57	6.1	[96]
N,*N*- dimethylamine-cyanoacetic acid	450, 478	12.9	0.71	0.74	6.8	[97]
Porphyrin	400–650	14.0	0.68	0.74	7.1	[98]
Zinc carboxyphtholocyanine	680	16.20	0.66	0.72	7.74	[96]
Coumarin	510	14.3	0.73	0.74	7.7	[99]
Oligothiophene	498	15.2	0.73	0.75	8.3	[100]
Oligo- phenylenevinylene TA-St-CA	386	18.1	0.74	0.67	9.1	[101]
Polypyridyl ruthenium complexe,N3	380, 530	11.5	0.70	0.74	10.3	[39]
Polypyridyl ruthenium complexe, Black Dye	605	20,53	0.72	0.70	10.4	[71]
Polypyridyl ruthenium complexe,N719	540	17.73	0.84	0.74	11.2	[102]
Polypyridyl ruthenium complexe,C101	547	5.42	0.74	0.83	11.3	[103]

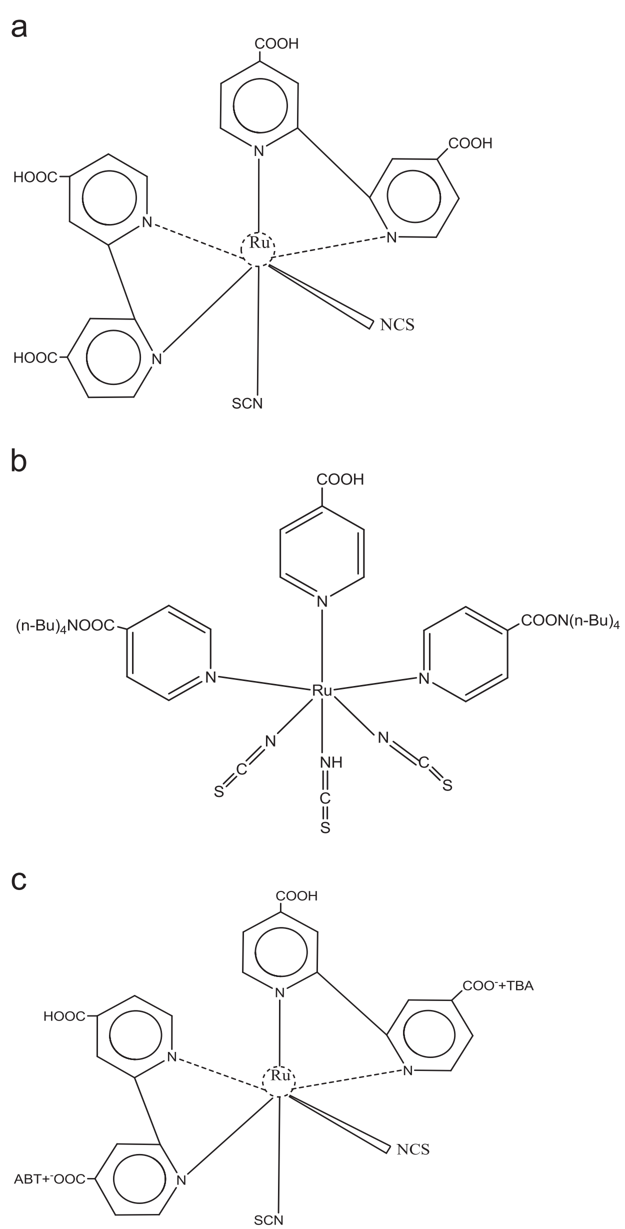


Fig. 4. Molecular structures of three efficient Ru dyes [70,71]. (a) N3, (b) N749 and (c) N719.

4. Efficiency measurement of DSSCs

The solar energy-to-electricity conversion efficiency (η) of DSSCs can be defined by the following conversion efficiency formula (Eq. 6) [60–65]:

$$\eta = \frac{P_{max}}{P_{in}} \tag{6}$$

where, P_{max} is the maximum output power and P_{in} is the input power (incident light) measured in $mWcm^{-2}$.

The fill factor (FF) of the DSSC is a measure of series resistance and junction quality of the cell, which can be defined using as follows (Eq. 7):

$$FF = \frac{P_{\max}}{J_{sc} \times V_{oc}} \tag{7}$$

where J_{sc} and V_{oc} are the short circuit currents (measured in $mAcm^{-2}$) and the open circuit voltage, respectively.

5. Photosensitizer

5.1. Commercial dye sensitizers

Given that dye has an important role in the absorption and conversion of solar energy to electricity, numerous researches have focused on molecular engineering of several organic metal complexes and organic dyes. Transition coordination complexes (Ru polypyridyl complexes) are employed as charge-transfer sensitizers, harvesting around 11% solar-to-electric energy in standard global air mass AM 1.5 of sunlight. These complexes are also one of the most effective sensitizers because of their high efficiency, excellent chemical stability, favorable photoelectrochemical properties, and intense charge transfer absorption in the wide visible range [66,67] (Table 1). However, Ru complexes contain a heavy metal that is harmful to the environment, aside from their complicated and expensive synthesis. Moreover, Ru complexes have the tendency to degrade in the presence of water [68,69,38].

Grätzel and his group developed many Ru complex photosensitizers [67]. The most famous among these complexes include the cis-bis(isothiocyanato)bis(4,4′-dicarboxylicacid-2,2′-bipyridine)Ru (II) coded as N3 or red dye (Fig. 4a); tris(isothiocyanato)-2,2′,2″-terpyridyl-4,4′,4″-tricarbolylate)Ru(II) complex, also referred to as black dye, coded as N749 (Fig. 4b); and di(tetrabutylammonium) cis-bis(isothiocyanato)bis(4-carboxylicacid-4′-carboxylate-2,2′-bipyridine) Ru(II), coded as N719 (Fig. 4c). These complexes

represent the most efficient sensitizers (~11%) because of their intense absorption range from the visible to the near-infrared region [70,71].

Regardless of their chemical stability and the possible exchange of charging with semiconducting solids, Ru complexes have large visible light-harvesting capacity, making them a judicious choice for the manufacture of solar energy conversion devices [72,73].

Several organic dyes and metal complexes use sensitizers, such as porphyrins, fluorescent dyes, platinum complex, and phtalocyanine [68]. The dyes, porphyrins, and phtalocyanine have attracted particular attention because of their phototherapeutic and photochemical applications [74]. However, porphyrins cannot compete with Ru dye sensitizer because of their low red and near infrared absorption. In the same spectral region, phtalocyanine shows inserted absorption. However, the problems with assembling the inappropriate active position of the LUMO level is that, it is very low for electron transfer to act as semiconductor for TiO_2 conduction band, which became tripled [37]. To obtain a broad absorption spectrum that extends to the visible and near infrared regions, another strategy that combines two mutually complementing dyes, such as porphyrins and phtalocyanine mixtures, in their respective spectrum can be used, which have already been applied to TiO_2 film [75,76].

An efficient photosensitizer has several basic fabrication requirements including: (i) strong dye adsorption particles onto the semiconductor surface; (ii) large visible light harvesting capacity; (iii) ability to inject the electron into the conduction band of the semiconductors; and (iv) finally, =O or − H groups capable of anchoring on the TiO_2 surface to ensure high rates of electron transfer [77–79]. Numerous researchers have focused on developing dyes as sensitizers in DSSC with highly applied specifications including: Ru (dcb)(bpy)$_2$ [80], Ru(bpy)$_2$(i-na)$_2$(PF$_6$)$_2$ [81], OsIII-bpa-Ru [82], and Ru (dcbH$_2$) [83]. Wang et al. studied the use of solar cell using the amphiphilic Ru sensitizer of cis-RuLL′(SCN)$_2$ (L=4,4′-dicarboxylic acid-2,2′-bipyridine, L'=4,4′-dinonyl-2,2′-bipyridine) [84]. The effects of the hydrophobic hydrocarbon chain length in amphiphilic Ru dyes on the efficiency of DSSC have been studied by Schmidt–Mende et al. [85]. Kuang et al. have reported an ion-coordinating sensitizer NaRu(4-carboxylic acid-4′-carboxylate)(4,4′-bis [(triethylene glycol methyl ether) methyl ether]-2,2′-bipyridine) (NCS)2 (coded as K51) with higher efficiency than a non-ion-coordinating analogy cis-Bis(isothiocyanato)(2,2′-bipyridyl-4,4′-dicarboxylato)(4,4′-di-nonyl-2′-bipyridyl)Ru(II) (coded as Z907) (η=7.8% and 3.8%, respectively) [86]. The new sensitizer Ru(4,4-dicarboxylic acid-2,2′-bipyridine) (4,4′-bis(2-(4-(1,4,7,10-tetraoxyundecyl)phenyl)ethenyl)-2,2′-bipyridine) (NCS)$_2$ or (K60) was developed by the prolongation of the pi system in the peripheral ligand (η=8.4%) [87]. A new ion-coordinating Ru polypyridyl sensitizer, NaRu (4-carboxylicacid-4′-carboxylate) (4,4′-bibis [(triethyleneglycolmethylether)heptylether]-2,2′- bipyridine) (NCS)$_2$, was developed by Kuang et al. (η=6.6%) [88]. Funaki et al. synthesized a new class of cyclometallated Ru (II) complexes Ru(tctpy) (C \widehat N)(NCS) (1, 2), where C \widehat N= is a bidentate cyclometallating ligand acting as sensitizers of light for DSSCs (η=2.2% and 3.7%, respectively) [89]. Kisserwan and Ghaddar developed a new cyclometallated Ru complex [Ru(6¢-phenyl-4¢-thiophen-2-yl-[2,2¢]bipyridinyl-4-carboxylic acid) (4,4¢,4¢¢-tricarboxy-2,2¢:6¢,2¢¢-terpyridine)]Cl, (T66), and reported it as a DSSC sensitizer (η=5.7%) [90].

5.2. Natural dye sensitizers

In nature, some flowers, leaves, and fruits show various colors and consist of several pigments that can be readily extracted and used for DSSC fabrication [104]. Natural pigments have been considered as promising alternative sensitizer dyes for DSSC because of their simple preparation technique, low cost, complete biodegradation, easy availability, purity grade, environmental friendliness, and most importantly, high reduction of noble metal, and chemical synthesis cost [105–107]. Plant pigmentation results from the electronic structure of pigments reacting with sunlight to change the wavelengths. The specific color relies on the capacities of the viewer. The pigment can be described by the maximum absorption wavelength (λ_{max}) [108].

The performance of natural dye sensitizer in DSSC has been evaluated by open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (FF), and energy conversion efficiency (η) [32] (see Table 2). Several pigments have been the famous subjects of research. Numerous natural dyes use sensitizers in DSSC, such as chlorophyll [66,109], carotenoid [30,105,110], anthocyanin [51,104], flavonoid [106,108,111], cyanine [112–114], and tannin [115]. Natural colorants are pigmentary molecules and dyes obtained mainly from plants, and perhaps, from animals or minerals, with or without chemical treatments. Natural colorants have a hydroxyl group in their structure and exhibit water solubility [43]. Several colorants do not have solubilizing group; hence, a temporary solubility group is generated during application [116].

5.2.1. Anthocyanin

The sensitization of wide band gap semiconductors utilizing natural pigments is often ascribed to anthocyanin. Anthocyanin belongs to a natural group that provides color to the flowers, fruits, and leaves of plants, and also responsible for several colors in the purple-red range [104,117]. Anthocyanin can also be found in other plant organs, such as tubers, roots, and stems [118], and are widely distributed in plant seeds. The molecular structure of anthocyanin is shown in Fig. 5a. Anthocyanin molecule have carbonyl and hydroxyl groups bound to the semiconductor TiO_2 surface, which excite electron transfer from the sensitizer (anthocyanin molecules) to the conduction band of porous TiO_2 film [66]. Anthocyanin extracted from different plants provides various sensitizing performances [112]. Polo et al. used the extracts of blue violet anthocyanin from Jaboticaba and Calafate as sensitizers. Solar energy cells sensitized by Jaboticaba extracts have been reported to achieve up to J_{sc}=9.0 mA cm^{-2}, V_{oc}=0.59 V, P_{max}= 1.9 mW cm^{-2}, and FF=0.54, whereas Calafate extracts can achieve up to J_{sc}=6.2 mA cm^{-2}, V_{oc}=0.47 V, P_{max}=1.1 mW cm^{-2}, and FF=0.36 [119].

Nishantha et al. fabricated a DSSC with an anthocyanin dye extracted from the barks of *Kopsia flavida* fruit, with the functional groups attached on the oxide semiconductor film, and showed J_{sc}=1.2 mA cm^{-2}, V_{oc}=520 mV, and FF=0.62 [107]. Khwanchi et al. extracted anthocyanin-rich natural dyes from the flowers of rosella (*Hibiscus sabdariffa* L.) and blue pea (*Clitoria ternatea*) as sensitizer of DSSC. They investigated the performance of the DSSC using mixed blue pea–rosella dye and hypothesized that two anthocyanin dyes having various absorption spectrums provided even more synergistic effect than the mixed chlorophyll–anthocyanin dye [43,120]. This result is due to the advantages of anthocyanin over the chlorophyll dye as a DSSC sensitizer [66,105]. Li et al. studied the photoelectrochemical optimal conditions for red cabbage extract as natural anthocyanin dye to improve DSSC [121].

5.2.2. Flavonoid

Flavonoid is the term that describes a great collection of natural dyes which includes a $C_6-C_3-C_6$ carbon framework, or more specially, phenylbenzopyran functionality [132] (Fig. 5b). Over 5000 naturally occurring flavonoids have been extracted from various plants, and divided according to their chemical structure

Table 2
Photoelectrochemical parameters of natural dyes based DSSC.

Dye	Semiconducting oxide	λ_{max} (nm)	J_{sc} ($mAcm^{-2}$)	V_{oc} (V)	FF	η (%)	Reference
Flowers							
Begonia	TiO_2	540	0.63	0.53	72.2	0.24	[32]
Rhododendron		540	1.61	0.58	60.9	0.57	
Marigold		487	0.51	0.54	83.1	0.23	
Perilla		665	1.36	0.52	69.6	0.50	
China loropetal		665	0.84	0.51	62.6	0.27	
Yellow rose		487	0.74	0.60	57.1	0.26	
Flowery knotweed		435	0.60	0.55	62.7	0.21	
Petunia		665	0.85	0.61	60.5	0.32	
Violet		546	1.02	0.49	64.5	0.33	
Chinese rose		516	0.90	0.48	61.9	0.27	
Rose		–	0.97	0.59	65.9	0.38	
Lily		–	0.51	0.49	66.7	0.17	
Hibiscus sabdariffa L.	TiO_2	520	1.63	0.40	0.57	0.37	[43]
Clitoria ternatea		580	0.37	0.37	0.33	0.05	
Erythrina variegata	TiO_2	451,492	0.78	0.48	0.55	–	[66]
Rosa xanthine		560	0.64	0.49	0.52	–	
Hibiscus surattensis	TiO_2	545	5.45	0.39	0.54	1.14	[122]
Nerium olender		539	2.46	0.40	0.59	0.59	
Hibiscus rosasinesis		534	4.04	0.40	0.63	1.02	
Sesbania grandiflora		544	4.40	0.41	0.57	1.02	
Ixora macrothyrsa		537	1.31	0.40	0.57	0.30	
Red *Bougainvillea glabra*	TiO_2	482,535	2.34	0.26	0.74	0.45	[123]
Violet *Bougainvillea glabra*		547	1.86	0.23	0.71	0.31	
Red *Bougainvillea spectabilis*		480	2.29	0.28	0.76	0.48	
Violet *Bougainvillea spectabilis*		535	1.88	0.25	0.73	0.35	
Fruits							
Tangerine peel	TiO_2	446	0.74	0.59	63.1	0.28	[32]
Fructus lycii		447,425	0.53	0.68	46.6	0.17	
Mangosteen pericarp		389	2.69	0.68	63.3	1.17	
Raspberries	TiO_2	540	0.26	0.42	64.8	1.50	[51]
Grapes		560	0.09	0.34	61.1	0.38	
Citrus sinensis (Red Sicilian)	TiO_2	515	3.84	0.34	0.50	–	[55]
Solanum melongena (Eggplant)		522	3.40	0.35	0.40	–	
Cheries	TiO_2	500	0.46	0.30	38.3	0.18	[64]
Capsicum	TiO_2	455	0.23	0.41	0.63	–	[66]
Kopsia flavida	TiO_2	550	1.20	0.52	0.62		[107]
Berberies buxifolia Lam (Calafate)	TiO_2	533	6.20	0.47	0.36	–	[119]
Myrtus cauliflora Mart (Jaboticaba)		520	7.20	0.59	0.54	–	
Hylocereus polyrhizus (Dragon fruit)	TiO_2	535	0.20	0.22	0.30	0.22	[124]
Wild Sicilian Prickly Pear	TiO_2	465	8.20	0.38	0.38	1.19	[125]
Chaste tree fruit	TiO_2	548	1.06	0.39	0.48		[126]
Mulberry		543	0.86	0.42	0.43		
Cabbage-palm fruit		545	0.37	0.44	0.61		
Ivy gourd fruits	TiO_2	458,480	0.24	0.64	O.49	0.09	[127]
Leaves							
Herba artemisiae scopariae	TiO_2	669	1.03	0.48	68.2	0.34	[32]
Chinese holly		–	1.19	0.60	65.4	0.47	
Vernonia amygdalin (Bitter Leaf)	TiO_2	400	0.07	0.34	0.81	0.69	[34]
spinach	TiO_2	437	0.47	0.55	0.51	0.13	[65]
Ipomoea		410	0.91	0.54	0.56	0.28	
Festuca ovina	TiO_2	420,660	1.18	0.54	0.69	0.46	[67]
Brassica olercea (Red cabbage)	TiO_2	537	0.50	0.37	0.54	0.13	[74]
Allium cepa (Red onion)		532	0.51	0.44	0.48	0.14	
Punica granatum (Pomegranate)	TiO_2	412,665	2.05	0.56	0.52	0.59	[104]
Shiso	TiO_2	440,600	3.56	0.55	0.51	1.01	[109]
Jathopha curcas Linn (Botuje)	TiO_2	400	0.69	0.05	0.87	0.12	[128]
Lawsonia inermis (Henna)	TiO_2	518	1.87	0.61	0.58	0.66	[129]
Ficus reusa	TiO_2	670	7.85	0.52	0.29	1.18	[130]
Rhoeo spathacea		670	10.9	0.50	0.27	1.49	
Garcinia subelliptica		670	6.48	0.32	0.33	0.69	
Anethum graveolens	TiO_2	666	0.96	0.57	40.0	0.22	[131]
Parsley (Petroselinum crispum)		666	0.53	0.44	34.0	0.07	
Arugula		666	0.78	0.59	42.0	0.20	
Seeds							
Coffee	TiO_2	–	0.85	0.55	68.7	0.33	[32]
Oryza sativa L. indica (Black Rice)	TiO_2	560	1.14	0.55	0.52	–	[66]
Bixa arellana L. (achiote)	TiO_2	474	1.1	0.57	0.59	0.37	[110]
	ZnO		0.08	0.32	0.37	0.01	
Other							
Green algae	TiO_2	666	0.13	0.41	21.0	0.01	[131]
Kelp	TiO_2	670	0.43	0.44	0.62	–	[130]

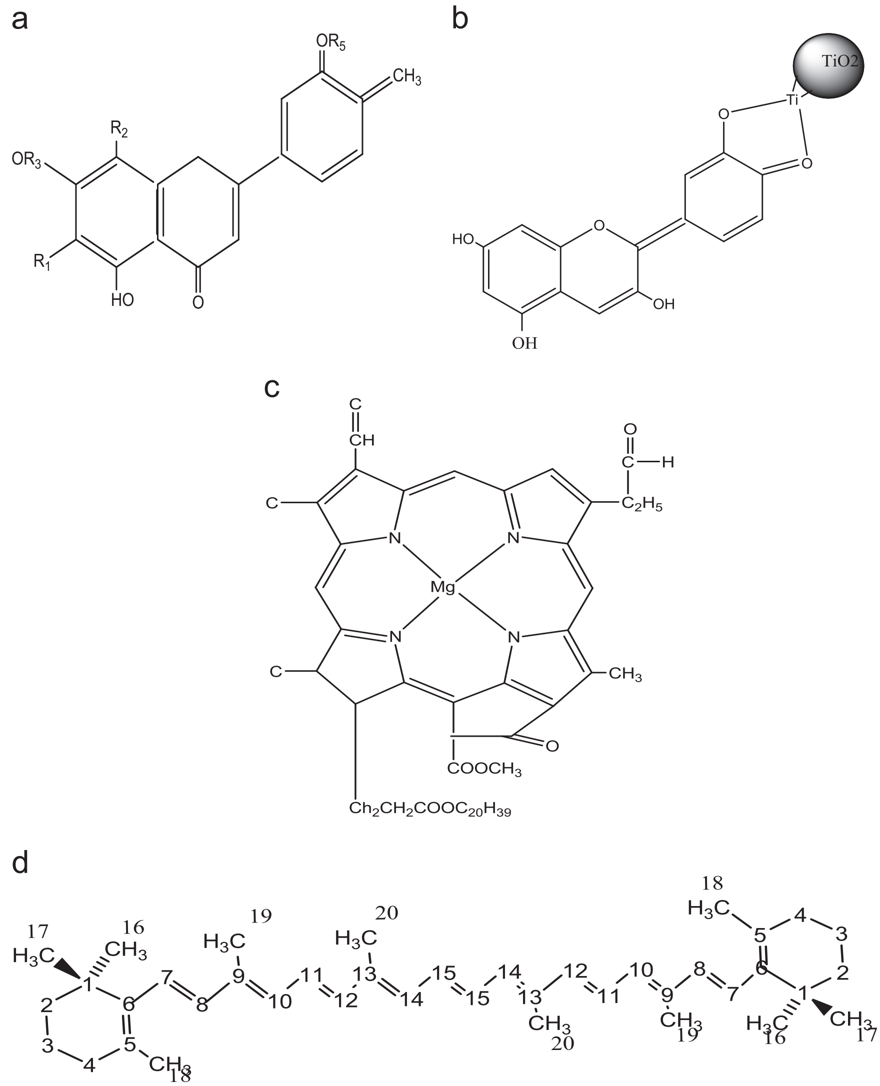


Fig. 5. The chemical structure of (a) anthocyanin, (b) flavonoid, (c) *β*,*β*-carotene, (d) chlorophyll.

as follows: flavonols, flavones, flavanones, isoflavones, catechins, anthocyanin, and chalcones. Flavonols are divided into three classes: flavonoids (2-phenylbenzopyrans), isoflavonoids (3-benzopyrans), and neoflavanoids (4-bezopyrans). Flavonoids contain 15-carbon (C_{15})-based structure with two phenyl rings connected by three carbon bridges, forming a third ring. The degree of phenyl ring oxidation (C-ring) identifies the different colors of flavonoids. However, not all flavonoids have the ability to absorb visible light, although they have similar structures. Flavonoid molecules are characterized by loose electrons; thus, the energy required for electron excitation to LUMO is lowered, allowing pigment molecules to be energized by the visible light. The various flavonoid pigment colors are determined by the property wavelengths of the visible light absorbed by pigment molecules and those that are reflected. The adsorption of flavonoid to the mesoporous TiO_2 surface is fast, displacing an OH counter ion from the Ti sites that combines with a proton donated by the flavonoid structure [133]. Flavonoid pigmentation is based on the primary and secondary structures of flavonoids, and influenced by pH and the structures arising from self-association and inter and intramolecular interactions [9]. The flavonoid dye extracted from Botuje (*Jathopha curcas* Linn) can be used as a DSSC sensitizer. This solar cell is sensitized to achieve up to Jsc 0.69 $mAcm^{-2}$, V_{oc} 0.054 V, and FF 0.87, with a cell conversion efficiency (η) of 0.12% [128].

5.2.3. *Carotenoid*

Carotenoid (Car) is an organic pigment that naturally occurs in plants and microorganisms. Carotenoids, flavonoids, and anthocyanin are often found in the same organs. Carotenoid pigments supply flowers and fruits with red, yellow, and orange colors, and are usually responsible for yellow to orange petal colors [105,108,134]. Cars are light-harvesting pigments and have important roles in photosynthesis protection [58]. Car pigments complement chlorophylls through redox reactions. The raw natural dyes are better than those of the purified or commercial analogs because of the presence of natural extracts, such as alcohols and organic acids, which assist dye adsorption, prevent electrolyte recombination, and decrease dye accumulation. Hemalatha et al. reported that the conversion efficiency of the *Kerria japonica* carotenoid dye is 0.22% [135]. Cars are compounds consisting of eight isoprenoid units that are widespread in nature, and have great potential as energy harvesters and sensitizers for DSSCs (Fig. 5c) [136].

Theoretical achievements of the chemical and physical properties of natural dye as sensitizers are important in detecting the relationship between the performance and structure properties of dyes, as well as in the design and synthesis of new dye sensitizers [134,137]. Koyama et al. reported that the main factor for the increased cell performance is the reduced interaction among the

excited state dye sensitizers. A set of carotenoic-acid and retinoic-acid sensitizers have n-conjugated double bonds [138]. Yamazaki et al. studied natural carotenoids, crocetin, and crocin as DSSC sensitizers. The conversion efficiency of crocetin-sensitized DSCs (0.56%) is three times, or higher than crocin (0.16%), because of the presence of carboxylic groups in the crocetin molecule [31].

5.2.4. Chlorophyll

Chlorophyll (Chl) is a green pigment found in the leaves of most green plants, algae, and cyanobacteria. Six different types of Chl pigment exist, and the most occurring type is Chl α. The molecular structure includes a chlorine ring with Mg center, along with different side chains and a hydrocarbon trail, depending on the Chl type (Fig. 5d). Chl absorbs light from red, blue, and violet wavelengths, and derives its color by reflecting green.

Chls are the principal pigments in natural photosynthetic systems [58,139]. Their functions include harvesting sunlight, converting solar energy (to chemical energy), and transferring electrons. Chls include a group of more than 50 tetrapyrrolic pigments [140]. Chls and their derivatives are inserted into DSSC as dye sensitizers because of their beneficial light absorption tendency modes; the most efficient of which is Chl α (chlorine 2) derivative-methyl trans-3^2-carboxy-pyropheophorbide α. Xiao et al. reported that chlorine 2 has an ability to lead semiconductors TiO_2 and ZnO surfaces through different modes [141]. Chl has an absorption maximum at 670 nm because of an attractive compound that acts as a photosensitizer in the visible light range. Amao and Komor reported that the chlorine-e_6 (Chl-e_6) created by Chl hydrolysis contains three carboxylate groups in a molecule. Furthermore, Chls do not contain a heavy metal ion, and are thus suitable photosensitizers from the environmental viewpoint. The absorption spectrum of Chl-e_6 is similar to that of Chl. The J_{sc}, V_{oc}, and *FF* of the solar energy cell using Chl-e_6 adsorbed on TiO_2 film electrode are 0.305 $mAcm^{-2}$, 426 mV, and 0.45, respectively [142].

6. Issues on the stability of DSSCs

The stability of the four components of a DSSC, namely, dye sensitizer, counter electrode, electrolyte, and semiconducting oxide, has been subjected to close scanning. An ideal sensitizer for DSSC that is capable of converting standard global AM 1.5 sunlight to electricity should absorb all the sunlight below the threshold wavelength of about 920 nm. Thus, continuing scientific research that aims to further enhance the efficiency and long-term stability is required to fulfill the promises of future technology [143]. A DSSC device must remain applicable for 20 years without performance loss. The photostability of the DSSC sensitizer material must be capable of many redox cycles without decomposition, and must also have the ability to carry attachment groups, such as phosphonate or carboxylate, to promptly graft it to TiO_2 oxide [3]. The dye attachment group must spontaneously form a layer upon the oxide film. High probability dispersion of this molecular dye layer occurs upon photon absorption, and the relaxation of the dye molecule occurs when the excited electron is injected into the mesoporous conduction band. However, single dye monolayer absorption is weak; thus, producing a highly efficient sensitizing device is impossible, assuming that smooth substrate surfaces are imperative to avoid the recombination loss mechanism associated with polycrystalline (rough) structures in solid state photovoltaic. The barrier for charge recombination exists when the electron produced in semiconductor lattice is separated from the positive charge carriers by the dye molecule layer, which is an insulator in the ground state. Utilizing a roughness factor of over 1000 with nanocrystalline thin film has become the standard practice [144].

The best DSSC performance, where both conversions yield long duration stability, has been achieved with polypyridyl complexes of Ru and osmium developed by the Grätzel group, namely, N3, N719, and N747, aside from acquiring upper light harvesting properties and durability. The N3 dye as pure solid is stable in air even up 280 °C, where decarboxylation sets in. Upon prolonged illumination, N3 can sustain 10^8 redox cycles without remarkable lack of performance for up to 20 years of continuous operation in sunlight [145]. The very fast excited state deactivation of electron injected, which are into the semiconductor TiO_2 film occurs in femto-second time domain, causing its outstanding stability. Although the N3/N3$^+$ couples show reversible electrochemical behavior in various organic solvents, the oxidized state of the dye caused by electron injection is much less stable. Dye degrades through sulfur loss when maintained in the oxidized state. Considerable advantage of these dyes lies in the metal–ligand charge transfer transition through which the photoelectric charge is injected into a thin film. In Ru complexes, this transfer occurs at a much faster rate than the reverse reaction, in which the electron recombines with the oxidized dye molecule instead of flowing through the circuit and performing work [9,146].

Khwanchit et al. studied natural dyes extracted from rosella and blue pea flowers as a DSSC sensitizer, and reported that the conversion efficiency (η) of cell dye-sensitizer extracted from rosella (0.37%) was higher than that of a cell sensitizer from blue pea flowers (0.05%) because the high interaction between the dye (anthocyanin) in the rosella and TiO_2 leads to better charge transfer. Furthermore, the distance between the anthocyanin (cyanidin and delphinidin) skeleton and the point connected to the TiO_2 semiconductor surface is shorter than that of blue pea (ternatin) [43].

The structure of the dye used as sensitizer affects the stability, performance, and efficiency of DSSC, which occurs when the structure of the pigment has longer *R* group, leading to the emergence of steric hindrance for the pigment molecules to create a bond with TiO_2 surface. This process effectively prevents the molecule from arraying on the semiconductor TiO_2 thin film, thereby causing less electron transfer from the dye molecules to the TiO_2 conduction band [139].

The light absorption wavelength and the intensity of the dye also affect cell stability and performance. The type of solvent used in natural dye extraction also impacts the stability and performances of DSSC, as reported by Aduloju et al. in their study on natural pigment extracted from henna leaves (*Lawsonia inermis*) using different solvents [129]. The performance and stability of DSSC sensitizers are measured from extracts of different plant species, such as black rice, shiso leaf pigments [66], calafate fruits [119], henna [147], bamboo leaves [148], *Kopsia flavida* [107], gardenia fruit [30], raspberries, shami-berries, grapes, hibiscus [51], *Festuca ovina*, *Hibiscus sabdariffa*, *Tagetes erecta*, *Bougainvillea spectabilis*, and *Punica granatum* peel [67], *Bougainvillea glabra* and *Speectabilis* flowers [67], and eggplant (*Solanum melonena* L.) peels [114]; including 13 species, such as purple sweet potato (*Imomoea batatas* L.), mature bitter melon (*Momordica charantia* L.), yellow paprika (*capsicum annuum* L.), red cabbage (*Brassica oleracea* L.), Chinese foxglove (*Rehmannia glutinosa* Liboschitz), onion peel (*Allium cepa* L.), blue gardenia (*Gardenia jasminoides* Ellis) [149], and bitter leaf (*Vernonia amygdalin*) [33]; as well as 20 kinds of colorful pigments, such as mangosteen pericarp, violet, bauhinia tree, rose, *Herba artemisiae scopariae*, rhododendron, begonia, marigold, coffee [32], gardenia yellow [150], ivy gourd fruits, and red frangipani flowers [127].

Conclusions

Inorganic solid-state junction devices made of silicon are currently dominating the photovoltaic field and industry because of their cell efficiency. However, the dominance of these solid-state

junction devices is being challenged by the emergence of DSSCs. The use of natural dyes as sensitizers in DSSCs provided an alternative source because of their low cost, eco-friendliness, availability, and simple manufacturing and use. Recent developments on different kinds of sensitizers for DSSC devices have led to the use of natural dyes that absorb sunlight within the visible spectrum with higher efficiencies. The nature of the dye used as sensitizers is the main factor affecting the DSSC efficiency. The betalain pigment in red turnip extract recorded the highest efficiency of 1.70%. Although the stability and efficiency of this type of cells are still insufficient, they are expected to evolve soon because of the significant research efforts in developing all parts of the cell, especially, the sensitizers. The results of this study encourage further research on the use of new natural dye sensitizers to increase the efficiency and stability of DSSC for the market. Moreover, the new sensitizers should have the following characteristics: (1) higher redox cycles without undergoing decomposition; (2) ability to carry attachment groups, such as phosphonate or carboxylate, to absorb TiO_2; and (3) capability to absorb all the sunlight below the threshold wavelength of about 920 nm.

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